

US-PAT-NO: 6171343

DOCUMENT-IDENTIFIER: US 6171343 B1

TITLE: Ultra high molecular weight polyethylene components treated to resist shearing and frictional wear

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The present invention provides methods for modifying surfaces made from metal alloy and/or UHMWPE, preferably surfaces which are frictionally engaged, e.g., in an orthopaedic implant. The methods of the present invention reduce the coefficient of friction of the metal alloy component, reduce the shearing of fibrils from the UHMWPE component, and reduce sub-surface fatigue in the UHMWPE component. The method involves solvent immersion of the UHMWPE component to remove short chains of polyethylene at or near the surface of the component, and to swell and toughen the subsurface of the component. The method also involves firmly coating the surface of the metal alloy component with an adherent layer of diamond-like carbon ("DLC") by creating a metal-silicide interface at the surface of the metal alloy to permit firmer adhesion of DLC. Although the methods of the present invention are particularly useful in orthopaedic applications, the methods also can be used to treat similar components used in other applications.

The present invention relates to decreasing frictional wear and degradation in products, typically orthopaedic implants, in which components made from ultra-high molecular weight polyethylene (UHMWPE) come into frictional contact

with components, e.g., made of a metal alloy, such as cobalt-chromium.

The replacement of destroyed or damaged human joints is one of the great achievements of twentieth century orthopaedic surgery. However, total joint prostheses, composed of various combinations of metal, ceramic, and polymeric components, continue to suffer from distressingly limited service lives. For example, the current generation of high-load bearing prostheses for the hip and knee have a typical lifetime on the order of 6-12 years. Generally, failed implants can be replaced once or twice, which means that current technology provides a solution for--at most--about 25 years.

With human life expectancies steadily increasing, there is a driving need to increase significantly the effective lifetime of a single implant. One of the problems encountered in designing such prostheses is the difficulty of finding materials which are both biocompatible and also durable enough to replace a human joint. In use, a human joint is exposed to substantial, repetitive loads and frictional stresses.

Although the geometric details may vary, a natural human hip, knee, or shoulder joint generally includes: (a) a more-or-less spherical ball; (b) an attachment to a long bone; and, (c) a hemispherical socket (the "acetabular cup") in a contiguous bony structure which retains the spherical ball so that the long bone may pivot and articulate. In a healthy joint, nature minimizes the friction between the joint components and prevents bone-on-bone wear and destruction by using mating porous cartilaginous layers that provide "squeeze-film" synovial fluid lubrication. This lubrication results in a low coefficient of friction on the order of 0.02.

When a human joint has been destroyed or damaged by disease or injury, surgical replacement (arthroplasty) normally is required. A total joint replacement includes components that simulate a natural human joint, typically: (a) a more-or-less spherical ceramic or metal ball, often made of cobalt-chromium alloy; (b) attached to a "stem," which generally is implanted into the core of the adjacent long bone; and (c) a hemispherical socket which takes the place of the acetabular cup and retains the spherical ball. This hemispherical socket typically is a metal cup affixed into the joint socket by mechanical attachments and "lined" with UHMWPE so that the ball can rotate within the socket, and so that the stem, via the ball, can pivot and articulate.

The two other basic problems, which are coupled, are the subject of the present application. One of these problems, known as ball-cup friction and wear, results from frictional wear between the hemispherical bearing (which is "lined" with UHMWPE) and the polished spherical ceramic or metal ball attached to the stem. The other problem, known as sub-surface fatigue, results from brittleness of the UHMWPE bearing and the resulting tendency of the UHMWPE bearing to fail under reciprocating applied loads.

For many years, the acetabular cup in joint implants has been "lined" with UHMWPE, or other materials, in order to decrease the coefficient of friction of the socket or bearing. Unfortunately, clinical experience has shown that, at least when UHMWPE is used to line the bearing, either the surface of the UHMWPE "bearing" and/or the surface of the metal/ceramic ball ultimately is destroyed by friction-induced wear. Alternately, the acetabular cup loosens after a

period of use, greatly increasing ball-cup friction and wear.

Some insight into the cause of failure due to ball-cup friction and wear has been gleaned from histological studies of the surrounding tissue. These histological studies show that the surrounding distressed tissue typically contains extremely small particles of UHMWPE which range from sub-micrometers to a few micrometers in size. Larger particles of UHMWPE appear to be tolerated by the body, as is the solid bulk of the UHMWPE bearing. However, the body apparently does not tolerate smaller particles of UHMWPE. In fact, these small particles of UHMWPE cause powerful histiocytic reactions by which the body unsuccessfully attempts to eliminate the foreign material. Agents released in this process attack the neighboring bone to cause "wear debris-induced osteolysis" which, in turn, leads to a loss of fixation and loosening of the prosthesis due to "remodeling" of the bone.

The first step in the generation of the small particles of UHMWPE appears to be the formation of a very thin layer of polyethylene between the spherical ball and the UHMWPE lining of the bearing. This thin film of polyethylene adheres to the "ball" and serves as a soft, shearable, solid lubricant composed of millions of submicrometer particles. Adhesive wear between the ball and the bearing produces strong, adhesive junctions on the ball. When exposed to further friction, fibrils of the polymer shear off of these adhesive junctions and are drawn into slender connecting ligaments, eventually producing ligament rupture.

One way to reduce friction between the metal and UHMWPE components would be to

coat one or both of the components with diamond-like carbon (DLC), which is chemically inert, biocompatible, and is known to have a low coefficient of friction. Unfortunately, the very properties of DLC that make it a desirable coating for parts that will be frictionally engaged make it difficult to achieve strong adhesion of the DLC coating to the substrate, particularly where deposition temperatures must be low. This limited adhesion problem can be exacerbated by very high compressive stress, such as that found in a plasma-deposited DLC (up to 8 GPa). Therefore, some have concluded that DLC--or at least plasma-deposited DLC--cannot be used in orthopaedic applications.

Energetic ion beam-associated DLC has a far lower residual stress than plasma-deposited DLC, and is a better candidate for a high integrity DLC. The substrate material to which all forms of carbon adhere most successfully is silicon. This is because strong covalent Si--C bonds are easily formed between the coating and the silicon substrate. Some have attempted to improve the adhesion of DLC to other materials, such as metal alloys, by forming an interposed silicon bond-coat to which the DLC will adhere more strongly.

Unfortunately, this simple approach does not result in adhesion that survives in applications, such as orthopaedic applications, where the DLC coating is subjected to substantial friction and stress. The simple formation of a silicon bond-coat on a metal alloy appears to create another relatively weak interface between the silicon and the metal or alloy.

Therefore a method is needed by which a DLC coating can be strongly adhered to

a metal surface, and by which the shearing of polymer fibrils from an UHMWPE component can be prevented. The method would be most efficient if it rendered the UHMWPE compound less brittle so that sub-surface fatigue failure was reduced.

The present invention provides a method for modifying the surfaces involved, typically a metal alloy spherical ball and an UHMWPE bearing, to reduce: (1) frictional wear between such surfaces; (2) shearing of fibrils from the UHMWPE bearing; and (3) sub-surface fatigue in the UHMWPE component. The method involves solvent immersion of the UHMWPE component to remove short chains of polyethylene at or near the surface of the component, and to swell and strengthen the subsurface of the component. The method also involves treating the metal alloy spherical ball to create a metal-silicide interface which permits firmer adhesion of DLC and thereby reduces the coefficient of friction of said surfaces. Although the methods of the present invention are particularly useful in orthopaedic applications, the methods also can be used to treat similar components used in other applications.

Methods of manufacturing components made of UHMWPE are known. The process of the present invention preferably is performed after the component has been formed, but before insertion into an end product, such as the metal cup of a total joint prosthesis. The apparatus used to immerse the UHMWPE component is not critical to the present invention. For example, if desired, the UHMWPE component may be immersed in the solvent using a simple hand-held instrument.

DLC COATING OF METAL COMPONENT

The method for treating a metal alloy to provide a diamond-like coating (DLC) uses ion beam assisted deposition of silicon, followed by deposition of DLC. This method is believed to form strong interatomic bonds across the DLC coating-substrate interface. In order to knit the successive layers of metal-silicon-DLC together effectively, it is necessary to supply a bond-interface for the metal-silicon bond as well as for the silicon-DLC bond. Without limiting the present invention, it is believed that the present method achieves this result by forming strong interatomic bonds having a character that is intermediate between the type of bond that exists between the atoms in the metal and the type of bonds in the silicon. Preferably, a metal substrate is used that forms a strongly-cohesive silicide--that is, an intermetallic compound in which the bonding is partially metallic and partially covalent. Metal substrates that form strongly-cohesive silicides include cobalt, nickel, titanium, zirconium, chromium, molybdenum, tungsten, platinum, and palladium. Silicon also is known to react with carbon atoms in DLC to form silicon carbide. Thus, the gradient formed by the process described herein is metal/metal-silicide/silicon/silicon-carbide/DLC. The type of bonds found in this gradient are believed to be intermetallic bonds in the metal alloy substrate; partially metallic and partially covalent bonds between the metal and silicon in the layer of metal silicide; primarily covalent but somewhat metallic bonds in the layer of silicon, which cohesively bonds to the layer of metal silicide; covalent bonds between the silicon and carbon atoms in the DLC in a layer of silicon-carbide; and, covalent bonds in the layer of DLC, which cohesively bonds to the layer of silicon-carbide.

After conventional cleaning of the component to remove superficial contaminants, such as grease, the component is placed in a vacuum chamber that has been evacuated to a base pressure of preferably less than 10^{-5} torr. The component then is bombarded with ions, preferably argon ions, at an energy range between about 10-100 keV, preferably around 10 keV. This ion bombardment provides an effective means to remove some of the remaining adsorbed atoms from the surface.

The component preferably is simultaneously bombarded with an energetic beam of ions, preferably argon ions, at an energy range between 500 eV to 100 keV, preferably between 10-20 keV, in order to form a layer of metal silicide at the metal-silicon interface. Although argon ions are preferred, other suitable ions may be used, such as nitrogen, argon, hydrogen, silicon, methane, helium, or neon, having an energy between 500 eV to 100 keV, preferably 10-30 keV. The ion-to-atom ratio should be sufficient, preferably at least 1 ion to 10 silicon atoms, to form a layer of metal silicide at the metal-silicon interface.

Thereafter, the component is cooled to about 80.degree. C., preferably without removing the component from the vacuum chamber, and the diamond-like carbon (DLC) is deposited, preferably using energetic ion beam deposition techniques. The DLC preferably should be deposited by vaporizing a precursor, such as polyphenyl ether, and condensing the precursor onto the surface of the component using known means. At the same time, the component should be bombarded, either in a continuous or interrupted fashion, with an energetic beam of ions. Preferable ions are nitrogen, argon, hydrogen, silicon, methane,

helium, or neon, having an energy between 500 eV to 100 keV, preferably 10-30 keV. The procedure is continued until a thickness of DLC between about 100 nm-10 microns is achieved.

Evaluation of wear resistance and the associated coefficient of sliding friction was performed under realistic environmental but static loading conditions. Two types of wear were measured. First, the wear represented by loss of the coating from the substrate, which was quantified in terms of the number of cycles required to expose the substrate, or major portions thereof. This determination was most effectively made by microscopic observation, rather than by weight loss.

The environment of a natural joint (with synovial fluid) was simulated using bovine serum. Pin/plate materials were chosen based on a judgment that the constraints of the total joint design cause a localized sector of the femoral ball to describe a wide path within the socket of the acetabular component. Eventually, as seen in joint simulator experiments, a millimeter or more of polymer may be worn away, with no measurable loss of material by the metal or ceramic ball. Therefore, these tests utilized metal, ceramic, or coated metal pins run against coated or uncoated polymeric plates.

The virgin UHMWPE that was used in the following examples was obtained from Westlakes Plastic, Lenni, Pa. For purposes of the present study, gamma-ray sterilization was not performed. If such sterilization had been performed, then the sterilization process should have produced a marginal improvement of mechanical performance, as a consequence of cross-linking. Because the surfaces of polyethylene is scratched easily, all of the surfaces and materials

were kept scrupulously clean using a laminar air-flow cabinet. A Struers Rotopol polisher with a Pedamat head was used to polish the samples according to the procedure given in Table I:

The alloy was manufactured by Carpenter Technology, Houston, Tex., and had the following composition: cobalt 70/chromium 30, with a minor addition of molybdenum. After machining, the 10 mm diameter test pins were contoured at one end to a radius of 20 mm and polished by standard metallurgical techniques. The curvature was designed to prevent the edge of the pin from cutting into the surface of the polyethylene flat.

Wear testing was performed using the wear test machine described above. The temperature was maintained within the test chamber at 23 ± 0.1 degree C. by means of an external water bath. The chamber containing the sample plate was reciprocated beneath the stationary pin at 1 Hz over a sliding distance of 50.8 mm per cycle; both sliding speed and distance approximate that which obtains during service within a total hip joint. Cobalt-chromium-molybdenum and alumina pins were machined to a 20 mm radius (similar to that of typical femoral balls) and polished metallographically to obtain a surface finish of less than 0.05 μm R.s.a.

The desired test load, and that used for most experiments, corresponded to a stress level induced by normal body loads at a total hip interface. Since the articulating pin-on-plate wear surfaces did not conform to the degree of the actual prosthesis, the required equivalent stress loads were lower. In particular, using the measured plastic impression within a UHMWPE plate as a measure of contact area, the approximate equivalent (stress) load was 33.4N.

For CoCr-DLC against Decalin.TM.-treated polyethylene, as well as for CoCr-DLC against untreated polyethylene, wear virtually was zero for more than one million cycles; however, major wear was observed for CoCr against untreated UHMWPE. In addition, it was observed that wear of CoCr on highly polished UHMWPE only occurred following an incubation period of approximately 500,000 cycles, versus the immediate wear measured for CoCr against rough polished (commercial quality finish) polyethylene. Unfortunately, once wear begins, the wear can be so rapid that the cumulative wear volumes for rough and smooth surfaces are essentially equal by approximately 1.5 million cycles. Therefore, the advantage achieved by polishing alone is short-lived, and ultimately inconsequential, due to the devastating wear rate associated with fibrillar pullout/failure.

In both cases, wear surfaces exhibited fibrillar pullout and microfailure. These observations are quantified in FIG. 2, which shows actual wear rate and wear factors (wear volume normalized for load) for all cases. These wear rates and wear factors for the CoCr-UHMWPE cases are in close agreement with data generated under similar conditions and reported in H. A. McKellop, et al., "Wear Characteristics of UHMWPE," J. Biomed. Mater. Res., 12 (1978) 895.

For the minimal wear cases, a groove caused by creep deformation was produced in the plates, but no weight loss was measured. At 10^6 cycles, sliding contact surfaces of the Decalin.TM.-treated UHMWPE had become gently undulating, with fine-scale, very flat deformation (but not wear) markings superimposed on the undulations. The original surface was flat (no

undulations) and covered with fine-scale polish markings. The latter contrasts with the original polished surface of untreated polyethylene, which was characterized by fibrillar structures similar to those observed during equilibrium wear.

Although likewise characterized by zero measured wear for at least 1.25×10^6 cycles, the contact microtopography for smooth-polished DLC against CoCr-DLC had a markedly different appearance. Undulations were not so apparent, and material appeared to have been pulled out of the surface. However, high magnification study of these structures indicated that they were fairly flat, unlike the sharply-peaked, tensile-failure, fibrillar structures observed for uncoated CoCr against UHMWPE. This suggested that the forum landmarks probably did not yet correspond to wear (detachment from the substrate).

The results of the test, given in Table II, show that after 10^6 cycles, no fibrils were present at the wear surface of Decalin.TM. treated polyethylene:

A later batch of four CoCr pins was treated using a bond-coat of silicon. Silicon was chosen because (a) DLC is known to adhere better to silicon than any other substrate, which is attributed to strong SiC bonds formed at the interface, and (b) cobalt and, to a lesser extent, chromium are known to form silicides (CoSi , $\text{CoSi}_{0.2}$, $\text{CrSi}_{0.2}$) at the interface if the temperature exceeds about 300°C . This solid state reaction is known to be enhanced by ion assisted deposition, probably because energetic ions disrupt the surface oxide or other barriers to interdiffusion at the metal-silicon interface.

Therefore, a coating process was chosen which was an argon ion-assisted deposition of approximately 100 nm of silicon at 300.degree. C. The silicon was evaporated from an electron-beam heated hearth and the thickness was controlled by means of a quartz crystal film thickness monitor (Intellimetrix Ltd.). DLC was deposited, in a separate run. After initial ion bombardment in the vacuum chamber to remove the remaining adsorbed atoms from the surface, the alloy was heated to a temperature of 300.degree. C. The DLC thickness achieved was approximately 0.5 microns.

From the appearance of the DLC-UHMWPE contact surface, it appears that localized adhesion takes place as the DLC rider passes over the polyethylene surface, possibly pulling out the soft (lower molecular weight) constituent on a gradual cyclic basis. However, the adhesive contact force is insufficient to fail the pulled out microstructure, at least before 1.25.times.10.sup.6 cycles. The prewear structures shown above do not resemble the individual "mountain peak" topography associated with submicrometer particle production; therefore, it is possible that a different particle generation mechanism, hence a different particle size distribution, will prevail. Since osteolytic destruction of the bone-biomaterial interface is induced principally by submicrometer particles, the production of larger average size particles may result in reduced osteolytic destruction. The possibility for improvement seems greatest for DLC against solvent-immersed UHMWPE. Here, soft-phase fibrillation was eliminated, there is a high likelihood that wear can be postponed further, that the eventual wear mechanism and rate will be altered, and that the wear particle size distribution will correspond to larger

particles, i.e., on the order of the hard semicrystalline domains. Moreover, since Decalin.TM. penetrates a significant fraction of a millimeter into the UHMWPE, these effects should persist throughout the wear process.

1. An orthopaedic implant comprising a metal alloy component comprising

an amorphous carbon coating in frictional contact with a surface of a second component, said surface comprising ultra high molecular weight polyethylene, wherein said surface is substantially undamaged due to swelling and said surface is devoid of polyethylene fibrils that shear off during frictional wear for about one million cycles against a polished CoCr pin at a stress level equivalent to that induced by normal body loads at a total hip interface, wherein said surface is treated by a processing comprising:

immersing said surface in an organic solvent for a first amount of time and at a temperature sufficient to dissolve polyethylene fibrils that frictionally shear off during said frictional wear but insufficient to result in damage due to swelling of said ultra-high molecular weight polyethylene, said organic solvent being selected from the group consisting of an aromatic hydrocarbon, an alicyclic hydrocarbon, an aliphatic hydrocarbon, and a mixture thereof; and

wherein said metal alloy component is coated with amorphous carbon by a process comprising:

heating said metal alloy component to a first temperature;

in a vacuum, condensing onto said metal alloy component silicon in an amount sufficient to form an inner bonding layer of metal-silicide cohesively bonded

to an outer layer of silicon;

condensing a carbon precursor onto said outer layer at a second temperature, a pressure, and for a second amount of time sufficient to form a film of precursor molecules on said outer layer, wherein said second temperature and said pressure are sufficiently low that said carbon precursor is not vaporized off of said component;

2. An orthopaedic component comprising a surface comprising ultra-high molecular weight polyethylene,

wherein said component is substantially undamaged due to swelling and said surface is devoid of polyethylene fibrils that shear off during frictional wear for about one million cycles against a polished CoCr pin at a stress level equivalent to that induced by normal body loads at a total hip interface

wherein said orthopaedic implant comprises a metal alloy component comprising a metal selected from the group consisting of cobalt, nickel, titanium, zirconium, chromium, molybdenum, tungsten, platinum, palladium, and combinations thereof, wherein said metal alloy component is coated with amorphous carbon by a process comprising:

heating said metal alloy component to a first temperature;

in a vacuum, condensing onto said metal alloy component silicon in an amount sufficient to form an inner bonding layer of metal-silicide cohesively bonded to an outer layer of said silicon;

condensing a carbon precursor onto said outer layer at a second temperature, a pressure, and for a second amount of time sufficient to form a film of

precursor molecules on said outer layer, wherein said second temperature and said pressure are sufficiently low that said carbon precursor is not vaporized off of said component;

3. An orthopaedic implant comprising a metal alloy component comprising an amorphous carbon coating in frictional contact with a surface of a second component, said surface comprising ultra high molecular weight polyethylene, wherein said surface is substantially undamaged due to swelling and said surface is devoid of polyethylene fibrils that shear off during frictional wear for about one million cycles against a polished CoCr pin at a stress level equivalent to that induced by normal body loads at a total hip interface wherein said amorphous carbon coating further comprises nitrogen ions implanted therein.

4. An orthopaedic implant comprising a metal alloy component comprising

an amorphous carbon coating in frictional contact with a surface of a second component, said surface comprising ultra high molecular weight polyethylene, wherein said surface is substantially undamaged due to swelling and said surface is devoid of polyethylene fibrils that shear off during frictional wear for about one million cycles against a polished CoCr pin at a stress level equivalent to that induced by normal body loads at a total hip interface, wherein said surface is treated by a process comprising:

immersing said surface in an organic solvent for a first amount of time and at a temperature sufficient to dissolve polyethylene fibrils that frictionally shear off during said frictional wear but insufficient to result in damage due

to swelling of said ultra-high molecular weight
polyethylene, said organic
solvent being selected from the group consisting of an
aromatic hydrocarbon, an
alicyclic hydrocarbon, an aliphatic hydrocarbon, and a
mixture thereof; and